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INTL ISOCYANATE INST., INC.

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BAYER AG

Document Title

ANALYTICAL METHODS TO MONITOR AEROSOLS OF DIPHENYL METHANE DIISOCYANATE AT LOW CONCENTRATIONS WITH ATTACHMENTS AND COVER LETTER DATED 072287

Chemical Category

DIPHENYL METHANE DIISOCYANATE (101-68-8)

INTERNATIONAL ISOCYANATE INSTITUTE, INC.
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PARSIPPANY, NEW JERSEY 07054

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Office of Toxic Substances
Environmental Protection Agency
401 M Street, S.W.
Washington, D. C. 20460

Attention: 8(d) HEALTH and SAFETY REPORTING RULE (REPORTING)
May 1, 1987

Dear Sir or Madam:

As described at 40 C.F.R. 716.20(a) , the International Isocyanate Institute (III) submits the enclosed studies on behalf of its members to satisfy member reporting requirements under Section 8(d) of the Toxic Substances Control Act. These studies are on chemicals added to the 8(d) list on May 1, 1987. The studies are indexed by CAS numbers with chemical name, III identification number and title provided.

Attachment #1 is an indexed list of completed studies.

Attachment #2 is a compilation of the reports from the completed studies.

Attachment #3 is an indexed list of studies that are currently in progress.

Please refer to the III identification number in any communication regarding the report.

If the Agency needs further information, please do not hesitate to contact me.

Very truly yours,

R. K. Rigger
Managing Director

RKR/c
enclosures

86-870000615

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 101-68-8 Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-p-phenylene diisocyanate
4,4'-Methylenebis(phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
10000	Prepolymeric MDI (Biphenylmethane Diisocyanat) with and without added Phenyl Isocyanate (PhI) - one hour acute inhalation toxicity.
10005	Determination of the concentration of vapor generated from monomeric 4.4'-Diphenylmethane Diisocyanate (MDI) by a dynamic method.
10008	Two-day study into the relation between polymeric MDI concentration values obtained by a QCM-Cascade, HPLC and Colorimetry.
10010	Liquid Waste after TDI/MDI decontamination.
10012	Literature Study on Reaction of Isocyanates with Biological Materials.
10013	Report on fire hazard of Isocyanate chemicals.
10014	Report on fire hazard of Isocyanate chemicals.
10018	Analytical methods to monitor aerosols of Polymeric 4,4'-Diphenylmethane-diisocyanate (MDI) at low concentrations.
10019	Aquatic life study phase II, step 2 Accumulation of TDI, MDI, TDA and MDA in fish and their toxicity.
10022	Generation and monitoring of breathable aerosols of polymeric 4,4'-diphenylmethane-diisocyanate (MDI).

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS #101-68-8 Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-p-phenylene diisocyanate
4,4'-Methylenebis(phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
10026	Pre-polymeric diphenylmethane,4,4', diisocyanate (Petmar MDI) Pre-polymeric diphenylmethane,4,4', diisocyanate + phenyl isocyanate. 50 ppm. Pre-polymeric diphenylmethane,4,4', diisocyanate + phenyl isocyanate. 150 ppm. An experiment to investigate the relative sub-acute toxicity of the above substances in the rat by inhalation.
10050	Metabolism and toxicogenetics of Methylenedianiline.
10065	A study of the diffusion of MDI in rats contaminated via the respiratory system.
10074	Investigations on the microbial degradation of PU forams. Part II.
10075	Respiratory Sensitivity Study.
10076	Deposition of aerosol components on the hair of rats exposed to polymeric MDI aerosols.
10077	Acute inhalation toxicity study of polymeric MDI in rats.
10092	Biological action of TDI and MDI in water.
10129	Immunological aspects of Isocyanates.
10187	Isocyanates : Irritation and Hypersensitivity.
10188	Preliminary study on skin sensitization caused by MDI solutions.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 101-68-8 Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-p-phenylene diisocyanate
4,4'-Methylenebis(phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
10206	Aquatic life study Phase II, Step 2, Accumulation of TDI, MDI and their reaction products in Daphnia.
10223	TDI and MDI immunological studies. Summary report of research supported by the International Isocyanate Institute.
10234	Aquatic life study Phase II, Step 1. Biodegradation of TDI and MDI in the model river and marine water.
10243	Mortality among workers exposed to isocyanates. Feasibility Study.
10253	Sub-chronic (13 week) inhalation toxicity study of polymeric MDI aerosol in rats (part B2)
10258	Ecotoxicity of Toluenediisocyanate (TDI) Diphenylmethanediisocyanate (MDI) Toluenediamine (TDA) Diphenylmethanediamine (MDA)
10299	Aquatic Life Studies
10317	Production and control of breathable MDI aerosols for primal experiments.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 101-68-8 Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-p-phenylene diisocyanate
4,4'-Methylenebis(phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
10360	Generation of 4,4' Diphenylmethane Diisocyanate (MDI) vapour
10386	Pharmacokinetics of MDI after inhalation exposure of rats to labelled MDI.
10391	Skin sensitization by isocyanates.
10393	Study of the burning characteristics of isocyanate chemicals.
10439	Di-Isocyanate Induced Asthma - Reactions to TDI, MDI, HDI and Hisamine.
24298	Acute Inhalation Toxicity (LC_{50}) in the Male Albino Rat.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS #1321-38-6 Benzene, diisocyanatomethyl-(unspecified isomer)

III NUMBER	TITLE
10010	Liquid waste after TDI/MDI decontamination.
10012	Literature Study on Reaction of Isocyanates with Biological Materials.
10013	Report on fire hazard of Isocyanate chemicals.
10014	Report on fire hazard of Isocyanate chemicals.
10019	Aquatic life study phase II, step 2 Accumulation of TDI, MDI, TDA and MDA in fish and their toxicity.
10024	Tolylene di-isocyanate three week inhalation toxicity in the rat.
10033	Stack Emission Part B : Emitted TDI Gas Treatment with Activated Carbon.
10034	Stack Emission Part A : Emitted TDI Gas Treatment with Activated Sludge.
10035	The toxicity and carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks.
10040	Reaction of TDI with water and with wet sand.
10044	Emission of Tolylene Diisocyanate (TDI) and Tolylene Diamine (TDA) in flexible polyurethane foam production lines.
10045	Emission of Tolylene Diisocyanate (TDI) and amines.
10055	Preparation and evaluation of a system for exposing rats to Toluene Diisocyanate vapour.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
10057	Evaluation of a system for exposing hamsters to Toluene Diisocyanate vapour.
10064	A study of the diffusion rate of TDI in rats contaminated via the respiratory system.
10074	Investigations on the microbial degradation of PU foams. Part II
10075	Respiratory sensitivity study.
10089	Studies of Toluene Diisocyanate induced pulmonary disease.
10092	Biological action of TDI and MDI in water.
10094	Foam plant stack emission data.
10095	Stack Emission Part B : Emitted TDI Gas Treatment with Activated Carbon "Regeneration of Spent Activated Carbon".
10096	Stack Emission Part A : Emitted TDI Gas Treatment with Activated Sludge.
10098	Epidemiological study for effects of TDI.
10100	Histopathological observations on selected tissues of syrian hamsters exposed by inhalation to vapors of Toluene Diisocyanate (TDI) for 6 hours/day, 5 days/week for 4 weeks.
10116	Review of the incidence of rhinitis in rats exposed chronically to Toluene Diisocyanate vapour.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
10117	Review of the national toxicology program carcinogenesis bioassay of Toluene Diisocyanate.
10121	Toluene Diisocyanate (TDI) proposed exposure standard.
10129	Immunological aspects of Isocyanates.
10142	Toluene Diisocyanate acute inhalation toxicity in the rat.
10153	A 30-day repeated inhalation toxicity study of Toluene Diisocyanate (TDI) in laboratory animals.
10159	The fate of Toluene Diisocyanate.
10162	Epidemiological study for effects of TDI.
10163	Validation of MCM 4000 personal monitor and MCM 4100 integrating reader/recorder system.
10168	Summary of work carried out on FE-A-14 III - 1 by H. Sakurai and co-workers.
10169	The toxicity and carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks.
10175	Emission of Tolylene Diisocyanate (TDI) and Tolylene Diamine (TDA) in flexible polyurethane foam production lines.
10184	Immunological studies on TDI exposed workers. Part I.
10187	Isocyanates : Irritation and Hypersensitivity.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
10206	Aquatic life study Phase II, Step 2, Accumulation of TDI, MDI and their reaction products in Daphnia.
10208	The Toxicity and Carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks. Addendum Report. Vol. 2.
10210	The Toxicity and Carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks. Vol. I
10223	TDI and MDI immunological studies. Summary report of research supported by the International Isocyanate Institute.
10233	The Toxicity and Carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks. Addendum Report. Vol. 1
10234	Aquatic life study Phase II, Step 1. Biodegradation of TDI and MDI in the model river and marine water.
10237	Isocyanate monomer in PU foam.
10243	Mortality among workers exposed to isocyanates. Feasibility Study.
10258	Ecotoxicity of Toluenediisocyanate (TDI). Diphenylmethanediisocyanate (MDI) Toluenediamine (TDA). Diphenylmethanediamine (MDA)
10259	Sampling and Analysis of TDI atmospheres at Klinikum Grosshadern, Munich.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
10299	Aquatic Life Studies.
10307	Studies on the effects of TDI on living animals.
10308	Change of TDI in olive oil.
10321	Improvement in RAST for TDI. Parts A and B.
10340	Audit of the national toxicology program carcinogenesic bioassay of toluene diisocyanate.
10345	Isocyanate spillage control.
10348	Immunological Studies on TDI exposed workers Part II.
10349	Isocyanate hypersensitivity.
10382	The toxicity and carcinogenicity of Toluene Diisocyanate vapour when administered to mice over a period of approximately 2 years. Summary Report.
10383	The toxicity and carcinogenicity of Toluene Diisocyanate vapour when administered to mice over a period of approximately 2 years.
10391	Skin sensitization by isocyanates.
10393	Study of the burning characteristics of isocyanate chemicals.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS #1321-38-6 Benzene, diisocyanatomethyl-(unspecified isomer)

III NUMBER	TITLE
10416	Sampling and analysis of TDI atmospheres at Klinikum Grosshadern, Munich.
10430	Protective effect of drugs on late asthmatic reactions and increased airway responsiveness induced by Toluene Diisocyanate in sensitized subjects.
10433	The reactions of OH radicals with Toluene Diisocyanate, Toluenediamine, and Methylene Dianiline under simulated atmospheric conditions.
10434	Metabolism and disposition of ^{14}C-labeled Toluene Diisocyanate (TDI) following oral and inhalation exposure ; Preliminary studies.
10437	Toluene Diisocyanate-Induced Asthma: Bronchial Provocation and Reactivity Studies.
10438	Toluene Diisocyanate-Induced Asthma: Inhalation Challenge Tests and Bronchial Reactivity Studies.
10439	Di-Isocyanate Induced Asthma- Reactions to TDI, MDI, HDI and Histamine.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 91-08-07 Benzene, 1,3-diisocyanato-2-methyl
TDI, 2-6-diisocyanate

III NUMBER	TITLE
24207	Disposition of 2,6-Toluene Diisocyanate in Fischer 344 rats

ATTACHMENT #2

COMPILATION OF REPORTS FROM III FILES
(AS INDEXED IN ATTACHMENT #1)

These reports are in envelopes labeled Attachment #2 and are packaged, along with an envelope, addressed to:

Document Processing Center (TS-790)
Office of Toxic Substances
Environmental Protection Agency
401 M Street, S.W.
Washington, D. C. 20460

Attention: 8(d) HEALTH and SAFETY REPORTING RULE
(REPORTING) May 1, 1987

from:

International Isocyanate Institute, Inc.
119 Cherry Hill Road
Parsippany, New Jersey 07054

containing a transmittal letter for these documents.

ATTACHMENT #3

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 101-68-8 Benzene, 1,1'-methylenebis(4-isocyanato-
Methylenedi-p-phenylene diisocyanate
4,4'-Methylenebis (phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
E-A-8	Study of chronic toxicity and carcinogenicity of polymeric MDI aerosol in rats. Part C Study. Current work authorized to begin June 1985. To study chronic toxicity and carcinogenicity of polymeric MDI aerosol in rats. Data sought - Effect on animal tissues. Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time. CIVO Institution, Tno., Toxicology and Nutrition, Utrechtsewe 848, P.O. Box 306, 3700 A.J. Zeist, The Netherlands.
E-H-44	MDI sampling and analysis at CIVO Current work authorized to begin November 1984. To study consistency/comparability of various methods continuous/discontinuous for determining the composition of atmospheres in Study E-A-8 (Part C) above. Data sought - Analytical data on polymeric MDI aerosol atmospheres. Our current estimated completion date for this study is the first quarter 1989 It may be possible to complete this study before 1989; however, it may require more time. CIVO Institution, Tno., Toxicology and Nutrition, Utrechtsewe 848, P.O. Box 306, 3700 A.J. Zeist, The Netherlands.

ATTACHMENT #3

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
E-B-11	Epidemiological study of workers in U.K. flexible foam industries. Current work authorized to begin Mid 1978. To investigate whether working on flexible PU foam manufacturing plants gives rise to increased expectation of decrements in lung parameters above those due to ageing. Data sought - monitoring of exposed workers' and controls' lung parameters. Monitoring of airborne TDI (and on limited scale of tertiary aliphatic amine) in the workplace. Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time. Tynestead Limited, Tynestead House, 22 Camberley Drive, Bamford, Rochdale, Lancs, OL11 4 AZ, UK. and Medical Research Council, 20 Park Crescent, London, UK.

ATTACHMENT # 3

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
FE-AB-14	Epidemiological study of workers in Japan flexible foam industries. Phase V.

Current work authorized to begin August 1985.
To clarify relationship between TDI concentration and chronological change in pulmonary and respiratory symptoms of workers in PU foam plants. Data sought.
Monitoring of exposed workers' and controls' lung parameters.
Monitoring of airborne TDI in the workplace.
Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time.
School of Medicine, Keio University, Shinjuki-Ku, Tokyo, Japan.

ATTACHMENT # 3

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
E-E-22	Clean Stack Air Project Current work authorized to begin March 1980. To study ways in which TDI Emissior from flexible foam plants can be removed from exhaust gases by carbon absorption. Data sought - Concentrations of TDI at inlets and outlets of carbon absorption units. Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time. Dunlop (Now BTR, Silvertown House, Vincent Square, London, UK.
E-AB-40	An investigation into the mortality and cancer morbidity of production workers in the UK flexible polyurethane foam industry. Current work authorized to begin July 1987. To compare the mortality and cancer morbidity experience of production workers in UK flexible foam manufacturing plants with those of unexposed controls and of the population at large, and to determine, if appropriate, possible reasons for differing experiences. Data sought. Comparative Data on death and illness due to cancer, analysed statistically. Data sought. The expected date of termination of project is indeterminate since it depends on results found at different intervals. The first analysis will take place 1989. Cancer Epidemiology Unit, University of Birmingham, Edgbaston, Birmingham UK.

ATTACHMENT #3

INDEXED LIST OF STUDIES IN PROGRESS

CAS #1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
NA-E-24	Fate of airborn TDI (Part II)

Current work authorized to begin May 1984.
To determine the fate of airborne TDI and the effects of moisture, light, and atmospheric pollutants on TDI loss from the gas phase.
Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time.
Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201

NA-AB-26 Detecting delayed isocyanate sensitivity.

Current work authorized to begin May 1, 1987.
This research is being conducted to better detect delayed isocyanate sensitivity in persons exposed and/or sensitized to isocyanates. In 1986, M. Karol's work was directed towards identification of isocyanate-specific lymphocytes by class.
Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time.
Dr. M. Karol, University of Pittsburgh, 130 Desoto Street, Pittsburgh, Pennsylvania 15261

ATTACHMENT #3

INDEXED LIST OF STUDIES IN PROGRESS

CAS #1321-38-6 Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
NA-AB-43	Improvement of RAST tests for TDI

Current work authorized to begin May 1, 1987.
This research is being conducted to improve RAST (Radiolabeled Antibody Sorbent Technique) test for identifying exposure and sensitization to TDI. Additional mechanistic work on TDI sensitization is being conducted by Dr Brown. This includes studying proteins in TDI exposed animals.
Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time.
Dr W. E. Brown, Carnegie-Mellon University, Pittsburgh, Pa. 15261.

NA-AB-50 TDI Reprotoxicity

The teratology study was initiated in the 4th quarter of 1986.
The reproduction study was initiated in the 2nd quarter of 1987.
This project evaluates both the "Developmental Toxicity of Inhaled TDI in CD (Sprague-Dawley) Rats" and "Two-Generation Reproduction Toxicity of TDI in CD (Sprague-Dawley) Rats."
Our current estimated completion date for this study is the first quarter of 1989. It may be possible to complete this study before 1989; however, it may require more time.
Dr T. W. Tyl, Bushy Run Research Center, RD #4, Mellon Road, Export, Pennsylvania 15632.

I.I.I. Project EA 9, Phase II

ANALYTICAL METHODS TO MONITOR AEROSOLS OF POLYMERIC 4,4'-DIPHENYLMETHANE-DIISOCYANATE (MDI) AT LOW CONCENTRATIONS

Supplementary Report to Report on I.I.I. Project EA 9, Phase I, of August 25, 1980:

GENERATION AND MONITORING OF BREATHABLE AEROSOLS OF POLYMERIC 4,4'-DIPHENYLMETHANE-DIISOCYANATE (MDI)

Authors: Dr. M. Aufsatz, ZB FE-DZA
Dr. H. Scheiter, ZB FE-DZA

Co-Author: Dr. J. Keller, ZB FE-D

December 1981

1. Summary

The International Isocyanate Institute, Inc. commissioned further experiments to be carried out, in addition to the studies described in the report on the "Generation and Monitoring of Breathable Aerosols of Polymeric 4,4'-Diphenyl=methane-Diisocyanate (MDI)", dated 25th August 1980, phase I of I.I.I. Project EA-9, written by A. Bürkholz and P. Vogtel. These additional experiments were necessary because discrepancies had appeared between the gravimetrically (cascade impactor) and analytically (sampling with wash bottles) determined values. At the time, the differences were attributed to incomplete absorption in the case of the wash bottle samples.

The additional experiments showed that MDI aerosol is quantitatively collected both in the cascade impactor and in the wash bottle. Proof was obtained by means of photometric determination following the addition of Oil Red to the polymeric MDI used.

The findings by isocyanate-specific chromatography (TLC, HPLC) were not as high as those of the photometric determination. They are particularly distinct for low concentrations and have to be explained by partial reaction of isocyanate with components of air.

On the other hand, the gravimetric values obtained at low concentrations were higher than those obtained photometrically. This is due to components of the air used in aerosol production (water, dust).

2. Introduction

Follow-up experiments to the EA-9 report phase I were intended to explain how given MDI aerosols (to be used for toxicological investigations) can be defined and described by means of concentration determinations. The lower concentration range was to be observed with particular attention (pp. 58/59 of the report).

The aerosol was produced in the manner described in Section 3 of Part A of this report.

The EA-9 report phase I showed that successive reduction of the aerosol concentration (from 100 mg/m^3 to 1 mg/m^3) resulted in increasing deviations occurring between gravimetric determination (cascade impactor) and analytical methods of determination (e. g. total carbon, infra-red spectroscopy, TLC, HPLC). It was assumed in the phase I report that these deviations were attributable to incomplete sampling. The danger of this occurring is particularly great in the case of small aerosol particles, since the maximum value on the particle size distribution curve - as shown on p. 57 of the report - shifts within the given limits ($\leq$ 3 μm) from 1.6 μm at aerosol concentrations of approx. 50 mg/m^3, to 0.8 μm at approx.1 mg/m^3.

Accordingly, a greater number of small particles are present in the low concentration ranges.

The follow-up experiments described in this report (EA-9 phase II) provide an explanation for this inconsistency.

The following diagram (Fig. 1) shows the procedures used to describe isocyanate aerosols in terms of concentration and particle size in the experiments reported in this paper.

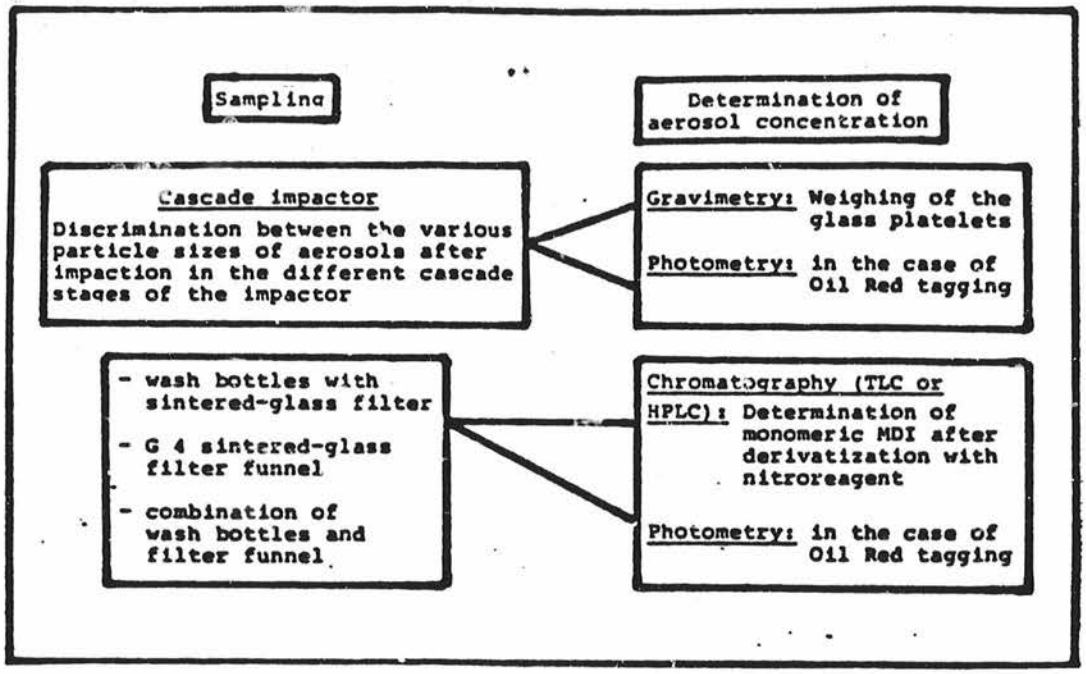
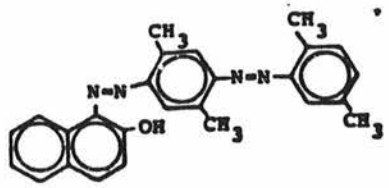


Fig. 1 Description of isocyanate aerosols in terms of concentration and particle size

The diagram above shows that, unlike the phase I report, photometry was used following the addition of Oil Red as a new measuring procedure of decisive importance for explanation purposes. The procedure was based on the following principle: the polymeric MDI to be aerosolized (in this case Bayer Desmodur 44 V 20) was marked with 0,5 % Oil Red in a preliminary stage (Fig. 2). This dye is chemically inert with respect to both air components and polymeric MDI, i.e. contrary to expectations, there is no reaction between the OH group of the Oil Red and the isocyanate.

Oil Red

Structural formula:



Molecular formula: $C_{26}H_{24}N_4O$

CA-Nomenclature: 2-Naphthalenol, 1-((4-((2,5-dimethylphenyl)-azo)-2,5-dimethylphenyl)azo)-

CA-Reg.-Nr. [4288-70-1]

Synonym: 1-((4-(xylylazo)xylyl)azo)-2-naphthol

Common names:
- C.I. 26125
- Oil Red OS
- D and C Red No. 18
- Oil Red O
- Oil Red 6B
- Oil Red 5B
- Orient Oil Red 5B

Application:
- Oil Red, analytical guide for inhalation toxicology studies
- Oil Red, petroleum dye, used to colour gasoline (preferential tax)

Fig. 2: Oil Red

Thus, as has already been demonstrated in previous experiments[1], Oil Red is suitable for use as a photometric guide with isocyanates, i. e. the dye quantity obtained photometrically is a direct measure for the polymeric MDI used.

3. Evaluation of the sampling system

Experience has shown that sampling with the cascade impactor yields quantitative results. By means of Oil Red tagging, it was possible to prove that quantitative collection of the aerosols succeeds

- with a G 4 sintered-glass filter funnel,
- with sintered-glass filter wash bottles and
- with a combination of both sampling devices,

the results using these equipments corresponded to those obtained for cascade impactor sampling.

This proof also holds good for low concentration ranges such as 1 mg/m^3. In spite of the quantitative collection during sampling thus proven, differing results were obtained for different methods of analysis.

4. Evaluation of the methods of analysis

The Oil Red method used to explain the quantitative collection of the aerosols has already been described above. In addition, the analytical methods listed in Fig. 1 were also used, the results of these being compared with those from the Oil Red method.

- Gravimetry was used to determine the total concentration of the aerosol and the particle size distribution via the cascade impactor.

- Chromatography (TLC or HPLC), following derivatization with nitroreagent (N-benzyl-N-propylamine)[2)3)], was used for the specific determination of isocyanate groups in the aerosol, via wash bottle and/or sintered-glass filter sampling. The calculation of the polymeric MDI content is accomplished via an evaluation of the monomeric MDI signal (TLC spot, HPLC peak) and extrapolation with the aid of the known monomeric MDI content (from GC) of the polymeric MDI used.

The results obtained using these processes have been numerically compiled in the enclosed table and are presented graphically in Fig. 3. The following comments can be made:

In the higher concentration range (approx. 60 mg/m^3), apart from random dispersion, only small relative differences can be observed between the gravimetric determinations and the other analytical values (photometry and chromatography).

In the 5 mg/m^3 range, and in particular in the 1 mg/m^3 range, the relative differences become larger; they become as more stringent as the aerosol concentration decreases.

In the case of the 5 mg aerosol, the gravimetric values are higher, but the chromatographic values lower than those from Oil Red photometry.

This is particularly distinct in the 1 mg experiment. Here, the level of the gravimetrically determined concentrations is approx. 40 % (relatively) higher than the results obtained from Oil Red photometry. The chromatographically determined values are 80 % (relatively) below these.

These findings can be plausibly explained as follows:

- The photometrically determined values (Oil Red) correctly reflect the set initial concentration in each case.

- The increase in the gravimetrically determined values in comparison to the photometrically determined values can be explained by the entrainment of air humidity and dust particles (note: the aerosol was produced in an open-air plant). It is obvious that the difference will increase with an increase in sampling time. At a concentration of approx. 1 mg/m^3, the sampling time must be approx. 120 minutes, in order to collect quantities in the cascade impactor which are large enough to be weighed. At concentrations of 5 mg/m^3 and 100 mg/m^3, sampling times were only 30 to 40 and approx. 15 minutes, respectively.

- The considerable differences between gravimetrically and photometrically determined values on the one hand and chromatographically determined values on the other hand, in particular in the case of low concentrations, can only be explained by a partial reaction of the isocanate groups of the MDI with air components, in particular with air humidity. This is supported by the observation that the solid part of the deposit on the cascade impactor platelets which is not soluble in tetrachloromethane is soluble in the more polar dichloromethane. It is a matter of fact that primary and secondary amines will react immediately with isocyanates to form ureas (sampling and analysis of the MDI-aerosols using the nitroreagent are basing on this reaction). Any amine which might be formed by hydrolysis of MDI can therefore not exist as such because it will react directly with excess MDI for urea which is crystalline.

It can be seen from the table that, viewed in absolute terms, the amount of MDI which reacts with air humidity is nearly constant and comparatively small for all concentrations. However, seen in relative terms, in the case of low concentrations this small quantity is of greater significance.

5. References

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2) J. Keller, K.L. Dunlap, R.L. Sandridge
"Determination of Isocyanates in the Working Atmosphere by Thin-Layer Chromatography"
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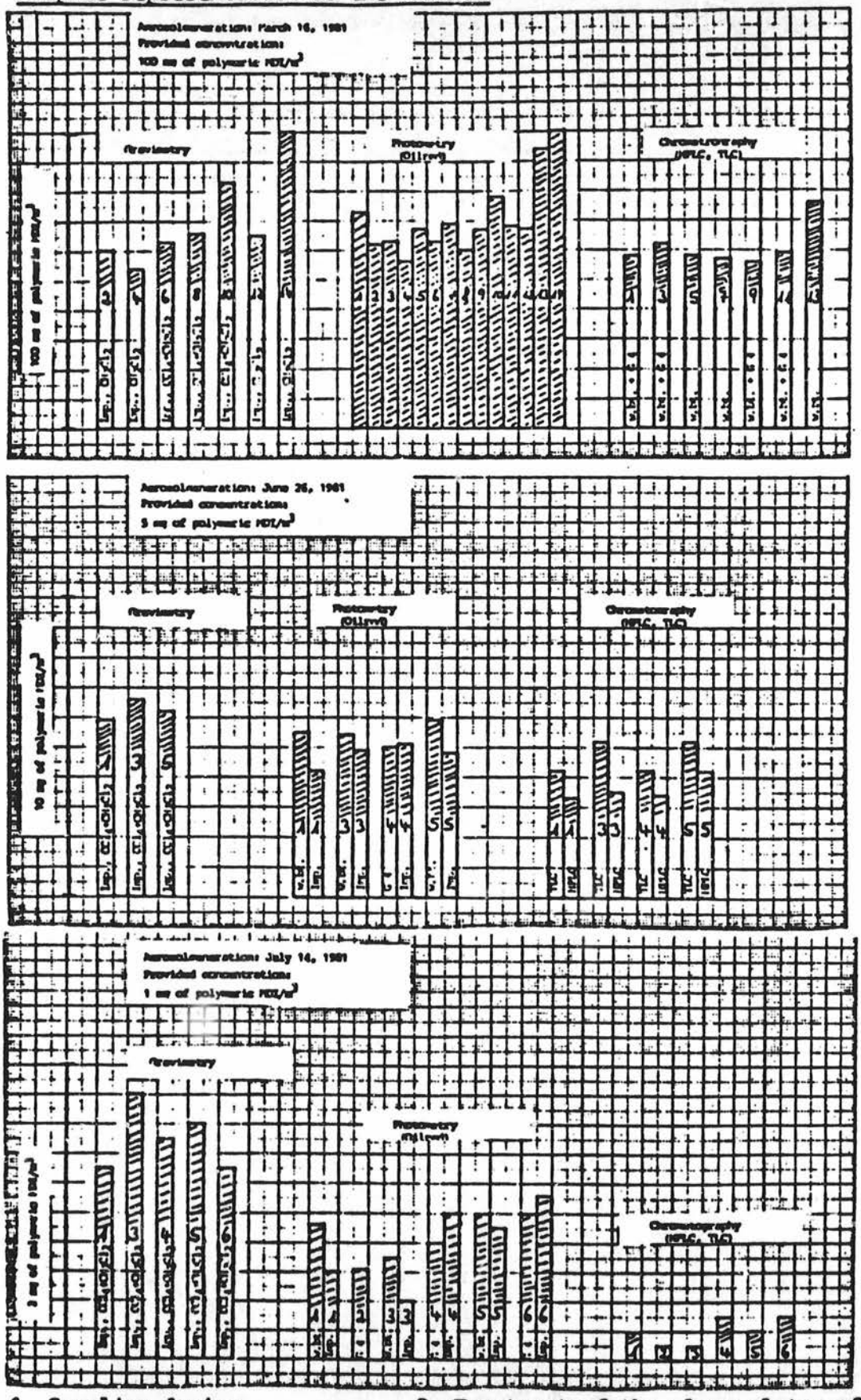
3) K.L. Dunlap, R.L. Sandridge, J. Keller
"Determination of Isocyanates in Working Atmospheres by High Speed Liquid Chromatography"
Anal. Chem. 48 (1976) 497

Figure 3

Graphic representation of the results



Notes

1. Sampling device

w.bt. = wash bottle
G 4 = G 4 sintered disc filter funnel
Imp. = cascade impactor

2. Treatment of the glass plates of the cascade impactor

CH_2Cl_2	in one step
CCl_4 + CH_2Cl_2	in two steps

Table of Results

Aerosolgeneration: March 16, 1931 Provided concentration: 100 mg of polymeric MDI/m^3				
	Gravimetry	Photometry (Oilred)	Chromatography HPLC	TLC
1	--	73	58	--
2	60	62	--	--
3	--	63	62	--
4	54	56	--	--
5	--	67	58	--
6	63	63	--	--
7	--	69	57	--
8	66	60	--	--
9	--	67	56	--
10	83	78	--	--
11	--	68	59	--
12	65	67	--	--
13	--	94	76	--
14	100	100	--	--

Aerosolgeneration: June 26, 1981 Provided concentration: 5 mg of polymeric MDI/m^3				
	Gravimetry	Photometry (Oilred)	Chromatography HPLC	TLC
1	--	5,5	3,3	4,2
1a	5,9	4,2	--	--
3	--	5,4	3,5	5,2
3a	6,6	4,9	--	--
4	--	5,0	3,4	4,2
4a	--	5,1	--	--
5	--	5,9	4,2	5,2
5a	6,2	4,8	--	--

Aerosolgeneration: July 14, 1981 Provided concentration: 1 mg of polymeric MDI/m^3				
	Gravimetry	Photometry (Oilred)	Chromatography HPLC	TLC
1	--	0,92	0,20	0,26
1a	1,3	0,60	--	--
2	--	0,63	0,10	0,18
2a	--	--	--	--
3	--	0,70	0,07	0,15
3a	1,8	0,40	--	--
4	--	0,80	0,28	0,38
4a	1,5	1,00	--	--
5	--	1,05	0,21	0,42
5a	1,6	0,90	--	--
6	--	1,03	0,30	0,42
6a	1,3	1,10	--	--
7	--	--	--	--

Notes:

1. Figures in the same line are resulting from the same sampling device, i. e. gravimetry + photometry from the cascade impactor and HPLC/TLC + photometry from the wash bottles and/or G 4 sintered disc filter funnel (porosity of 10 to 20 µm; there is no correlation between the porosity and the particle size of the aerosol to be collected).
2. The figures in the columns represent the deviation of the real measured concentration from the provided concentration.
3. Strucke (-) means no measurement.

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